Identifying the relevant biogeochemical processes at sites impacted by organic contaminants

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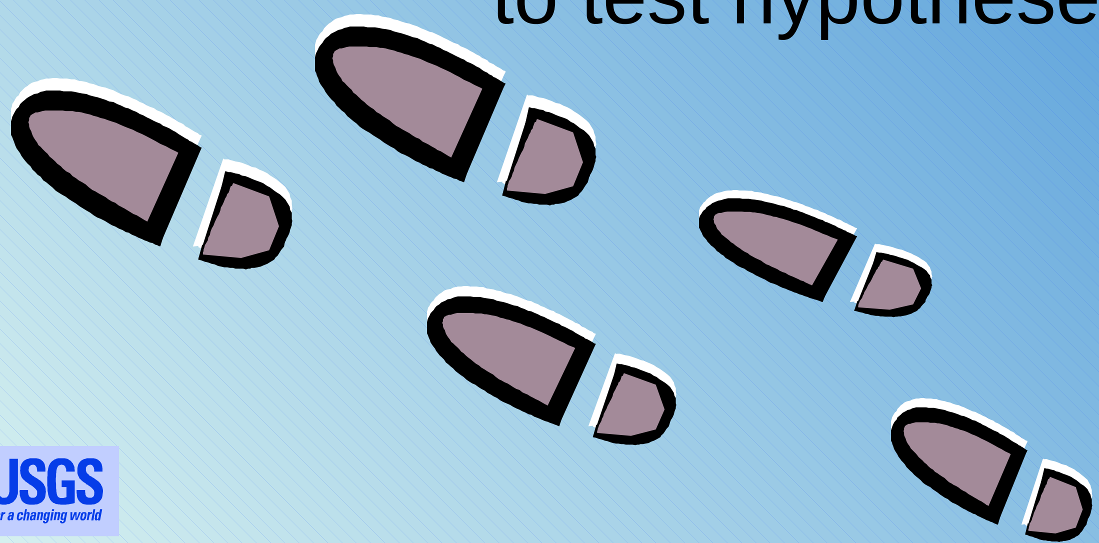
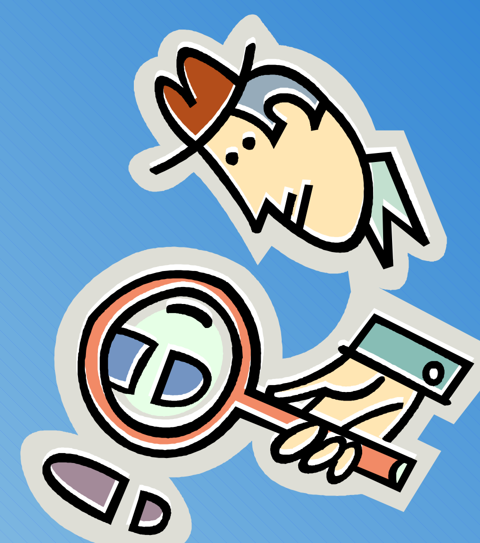
Fate of reactive contaminants depends on geochemical reactions in the subsurface.

When organic contaminants are involved these reactions are most often biologically mediated.

In complex systems, such as subsurface hydrogeologic environments, identifying all the biogeochemical reactions is difficult.

In order to determine which biogeochemical processes are most relevant we look for evidence, or footprints, of those processes. This can be loss of contaminants themselves or electron acceptors used during reactions or an increase in metabolites or end products produced during reactions. We look in the ground water, sediments, and soil gas at a range of spatial and temporal scales and conduct *in situ* experiments to test hypotheses.





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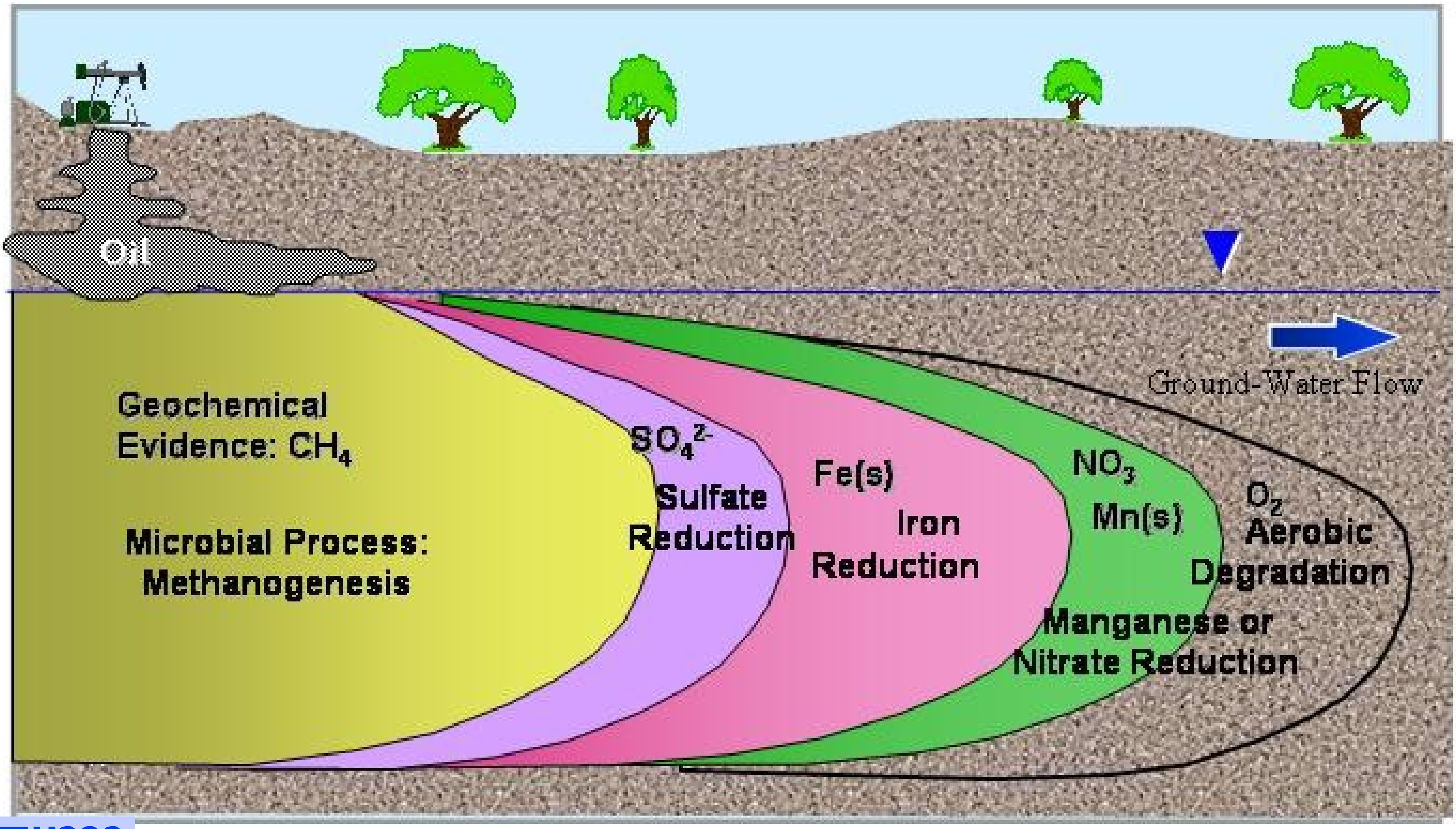
In the subsurface biogeochemical processes that control contaminant fate vary in space and time and alter the aquifer aqueous and solid phase chemistry



Geochemical Indicators of Biodegradation Processes

- Electron Acceptors

  O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, $CO_{2,}$ Mn(IV)s, Fe(III)s

- Electron Donors

  Organic substrate (natural or contaminant), Fe(II)s, NH_4^+

- Intermediates

  H_2, Organic Acids

- Reaction Products

  HCO_3^-, N_2O, NO_3^- NH_4^+, Fe^{2+}, Mn^{2+}, H_2S, CH_4, Fe(II)s

- Isotopic fractionation

  $\delta\ ^{13}C$, $\delta\ ^{15}N$, $\delta\ ^{34}S$, $\delta\ D$, $\delta\ ^{18}O$, $\delta\ ^{37}Cl$

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Geochemical Indicators of Biodegradation Processes

In assessing the dominant biogeochemical reactions in a subsurface environment contaminated with organic or mixed waste our experience at numerous field sites has shown us we need to consider many sources of these indicators including:

1. The aquifer solids
2. Water from outside the plume
3. Co-contaminants within the plume

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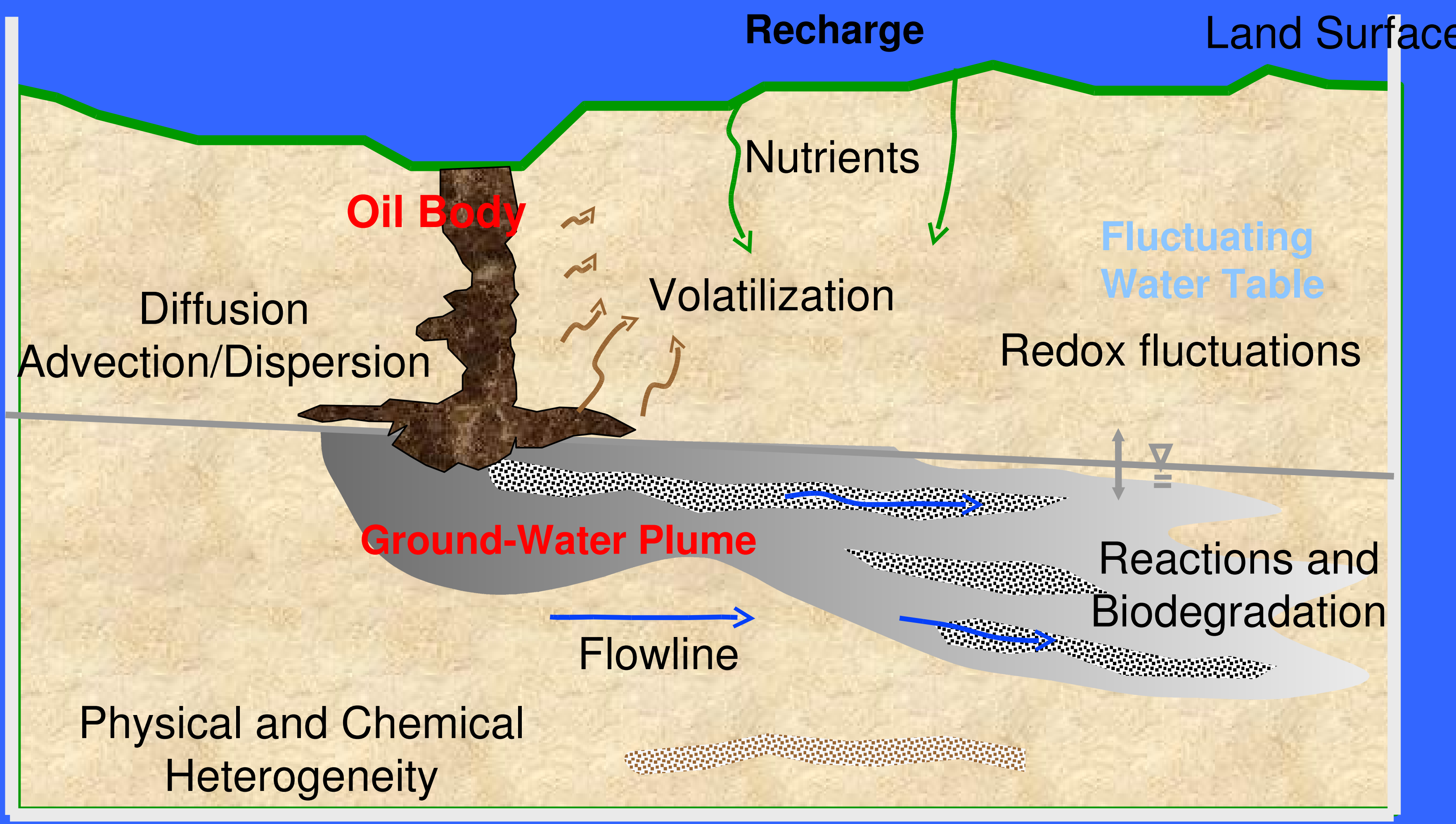
Biogeochemical Processes that Control Contaminant Fate are Influenced by the Complexity of the System



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We also need to understand the role of the microorganisms in the system and the feedback between the geochemical environment and microbial activity.

The value of long-term studies, such as those done at Toxics sites, is that we can track changes in the source of contamination and biogeochemical processes over time as reactions at these sites progress, making us better able to make informed choices about what we may need to look for at other sites.

Some Key Lessons Learned at Toxics Sites when Identifying Controlling Biogeochemical Processes Relevant to Contaminant Fate:

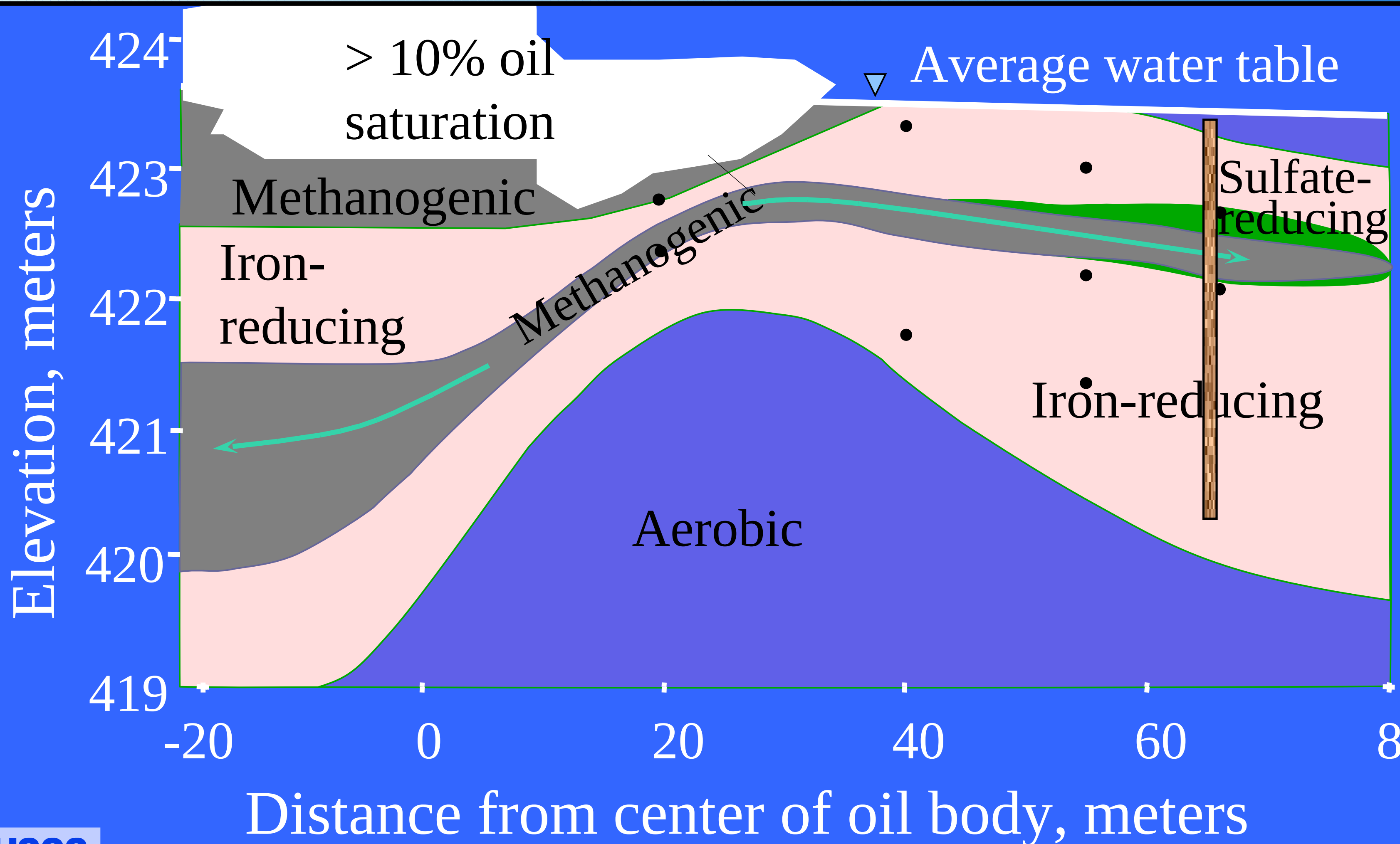
- Changes over time in aquifer geochemistry can control progress of reactions and in evaluating these changes it is essential to consider the solid phase
- Reactions at plume fringes and interfaces are especially important because these are often areas of chemical exchange
- Feedback between the geochemistry and *in situ* microbial community impacts potential for future biodegradation reactions

Example #1: Bemidji Crude Oil Spill

Crude oil infiltrated the subsurface and oil was found in water table wells

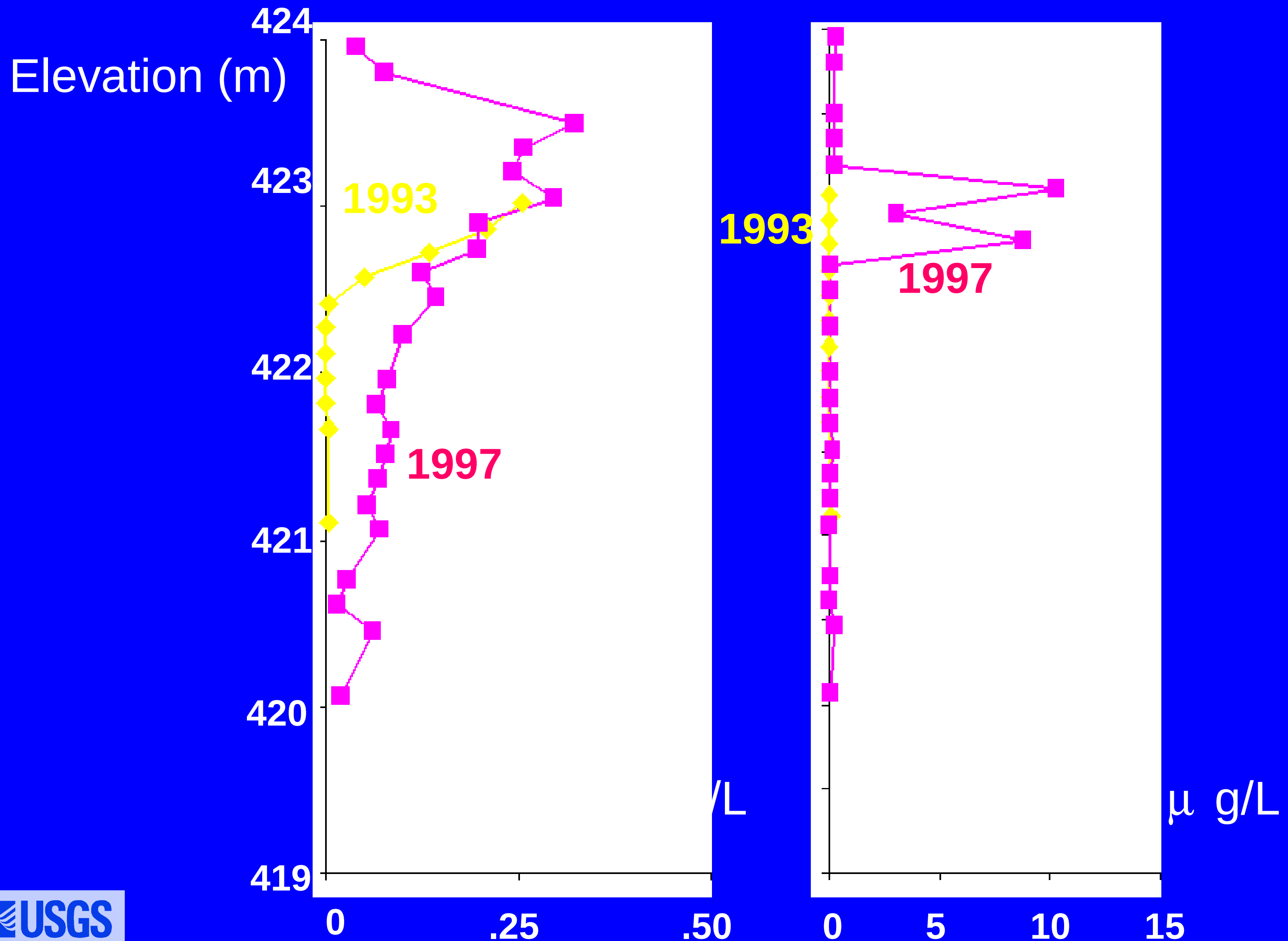
Monitoring wells were used for plume-scale observations. Smaller-scale samples were collected by extracting pore water from cores

The plume-scale observations were combined with cm-scale geochemical and microbial studies, revealing narrow redox zones that evolve over time on the scale of years to decades.



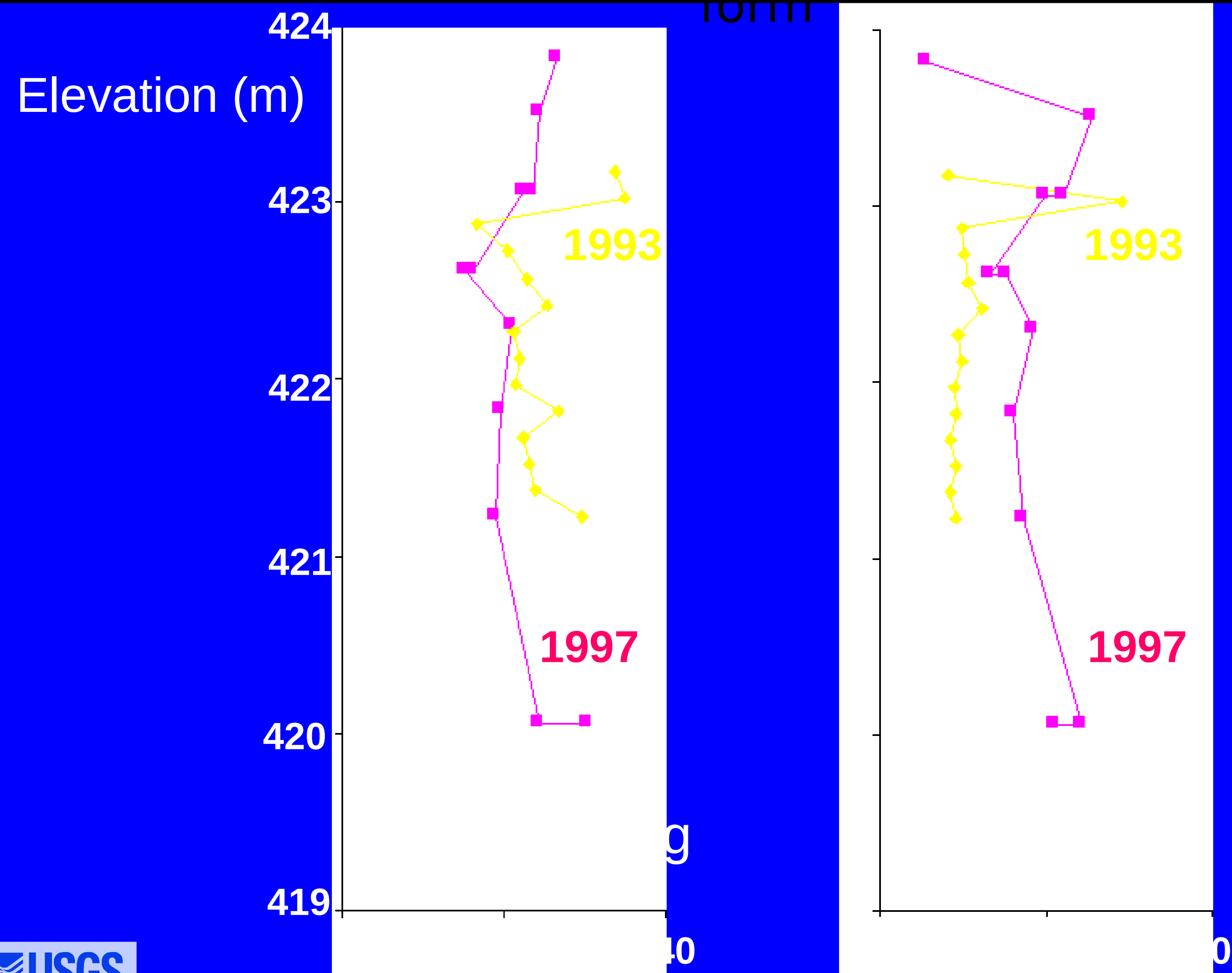
Bekins et al., Cozzarelli et al., JCH, 2001

Changes Over Time: By looking at the cm scale we found the plume is growing- ethylbenzene and *ortho*-xylene at edge of anoxic zone

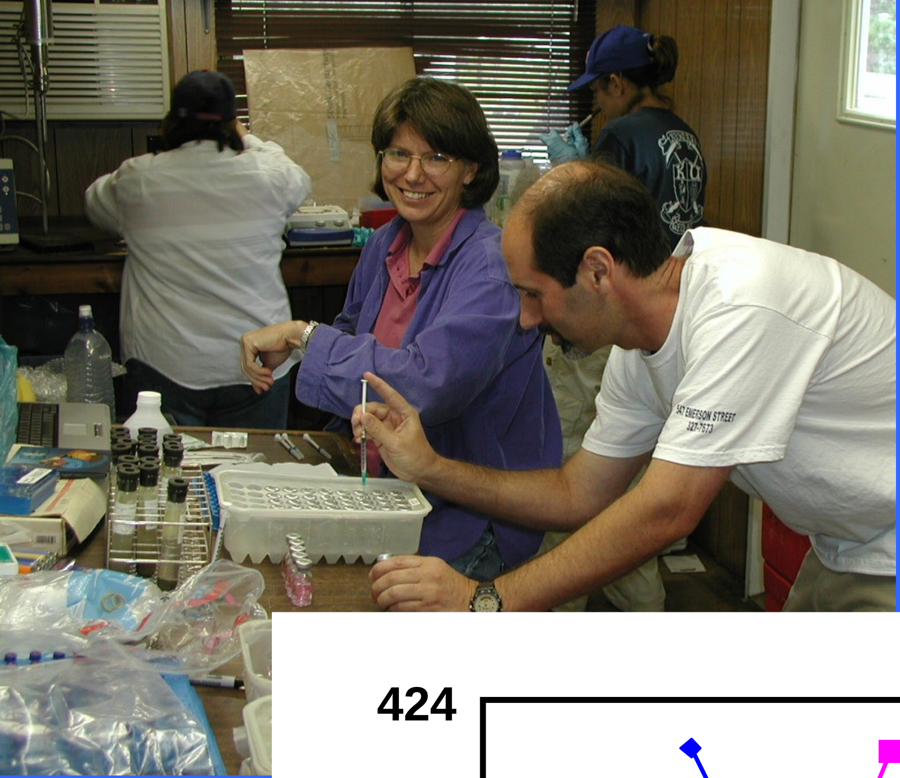


Cozzarelli et al. JCH (2001

Importance of solid phase Fe(III)s:
By looking at the sediment Fe at this same scale we could see the shift in redox state of the Fe from oxidized to reduced form

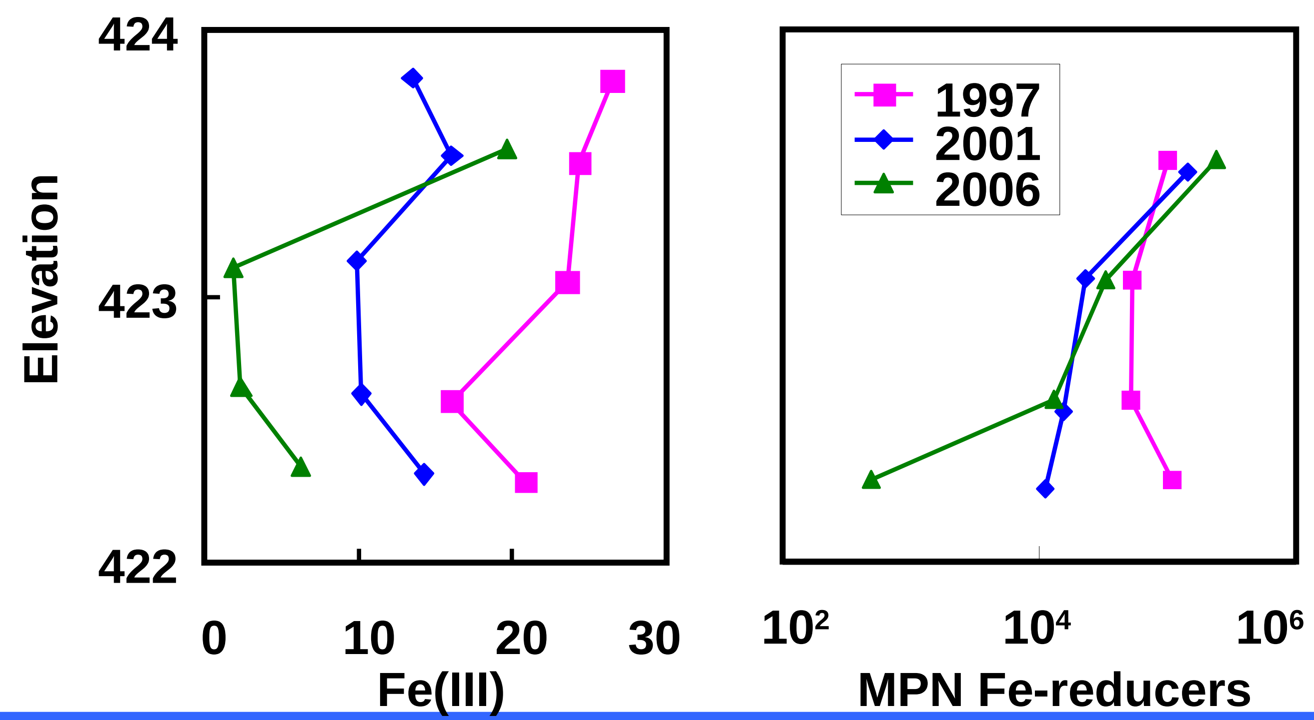


Cozzarelli et al. JCH (2001)



Relationship between microbes and minerals: Fe (III)s continues to be depleted at 65 m

Fe-reducer MPN's also decreased at 65 m from 1997-2006



Bekins et al., JCH, 2001

Example #2: Municipal Landfill Norman, OK

Landfill accepted unrestricted solid waste- closed in 1985
covered with clay and vegetation

The plume intersects a wetland

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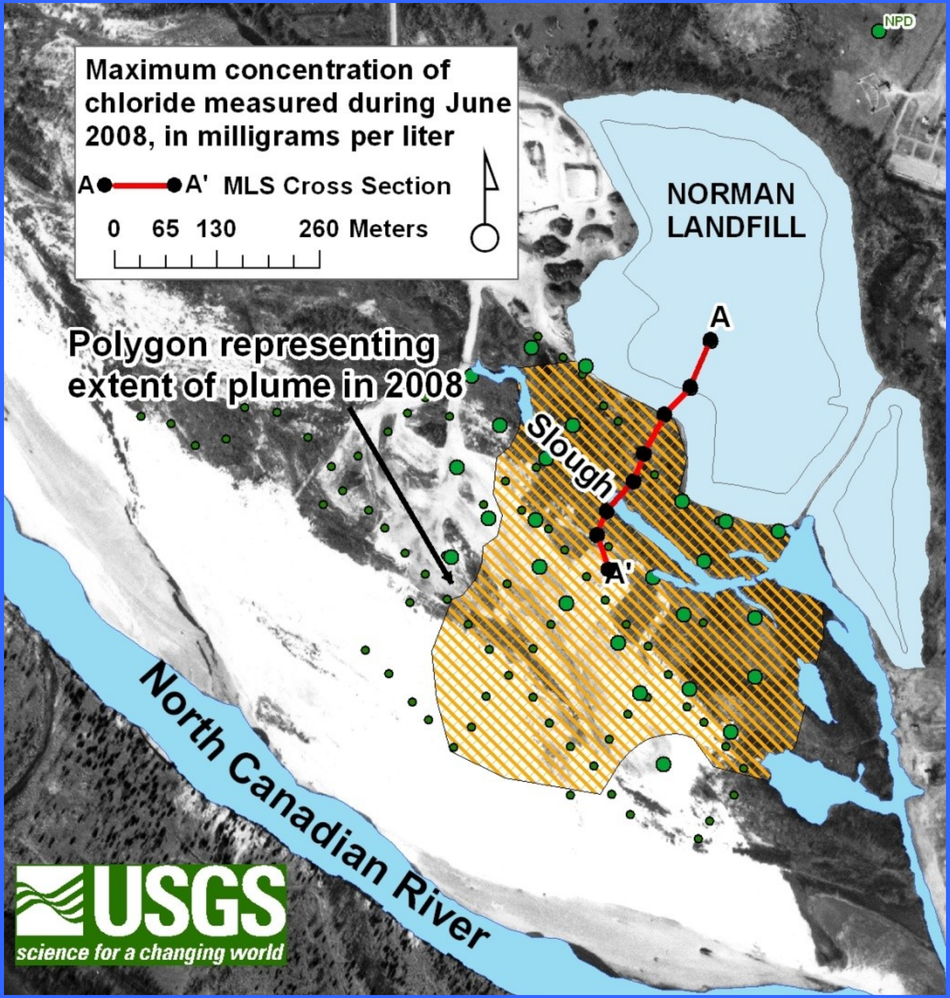
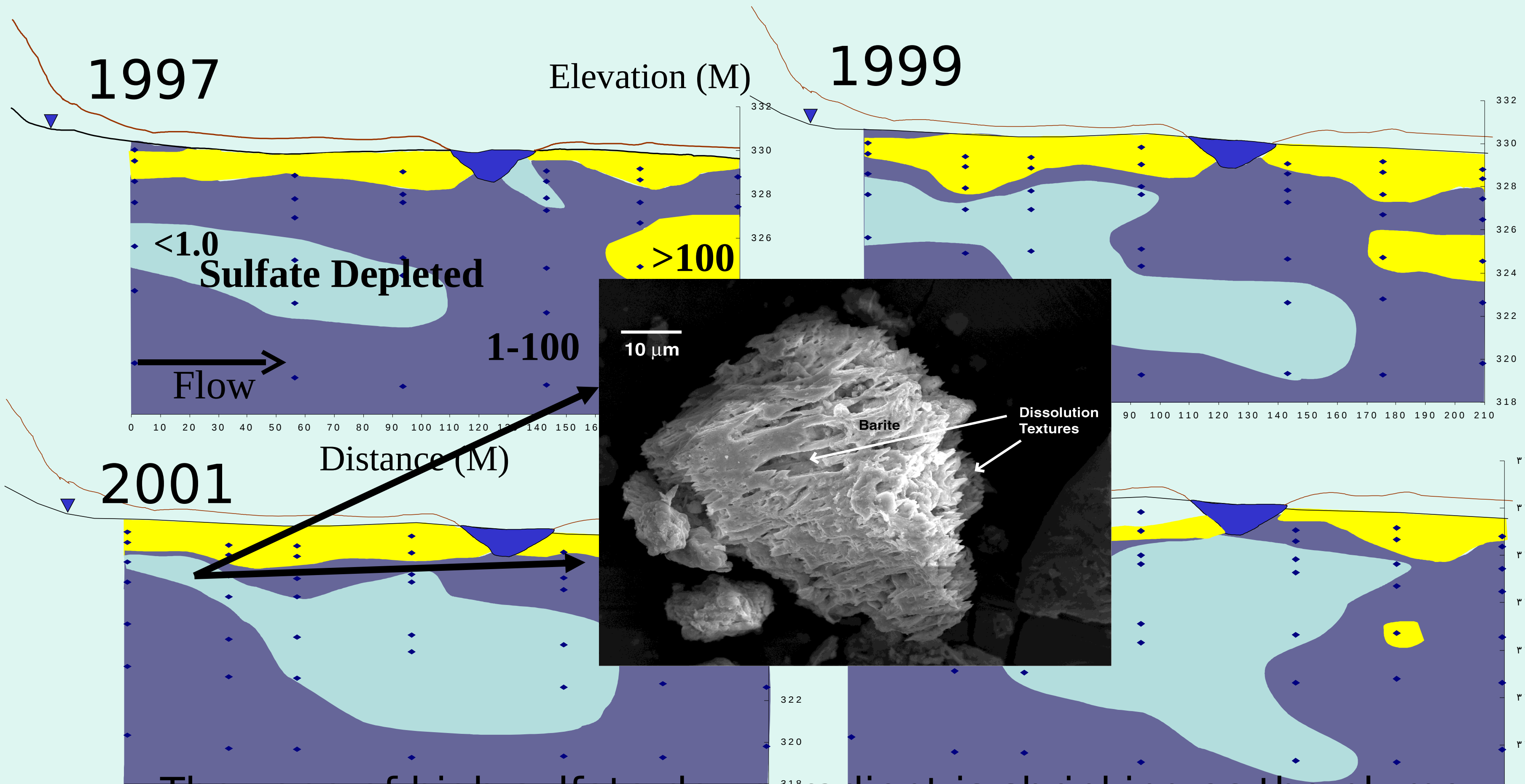
An anoxic plume containing high concentrations of DOC, chloride, ammonium, and other organic and inorganic species is migrating south underneath a wetland and toward the Canadian River.



Next Two Slides Show Temporal Changes in Geochemistry along the A-A’ transect.

Cozzarelli et al., ES&T,

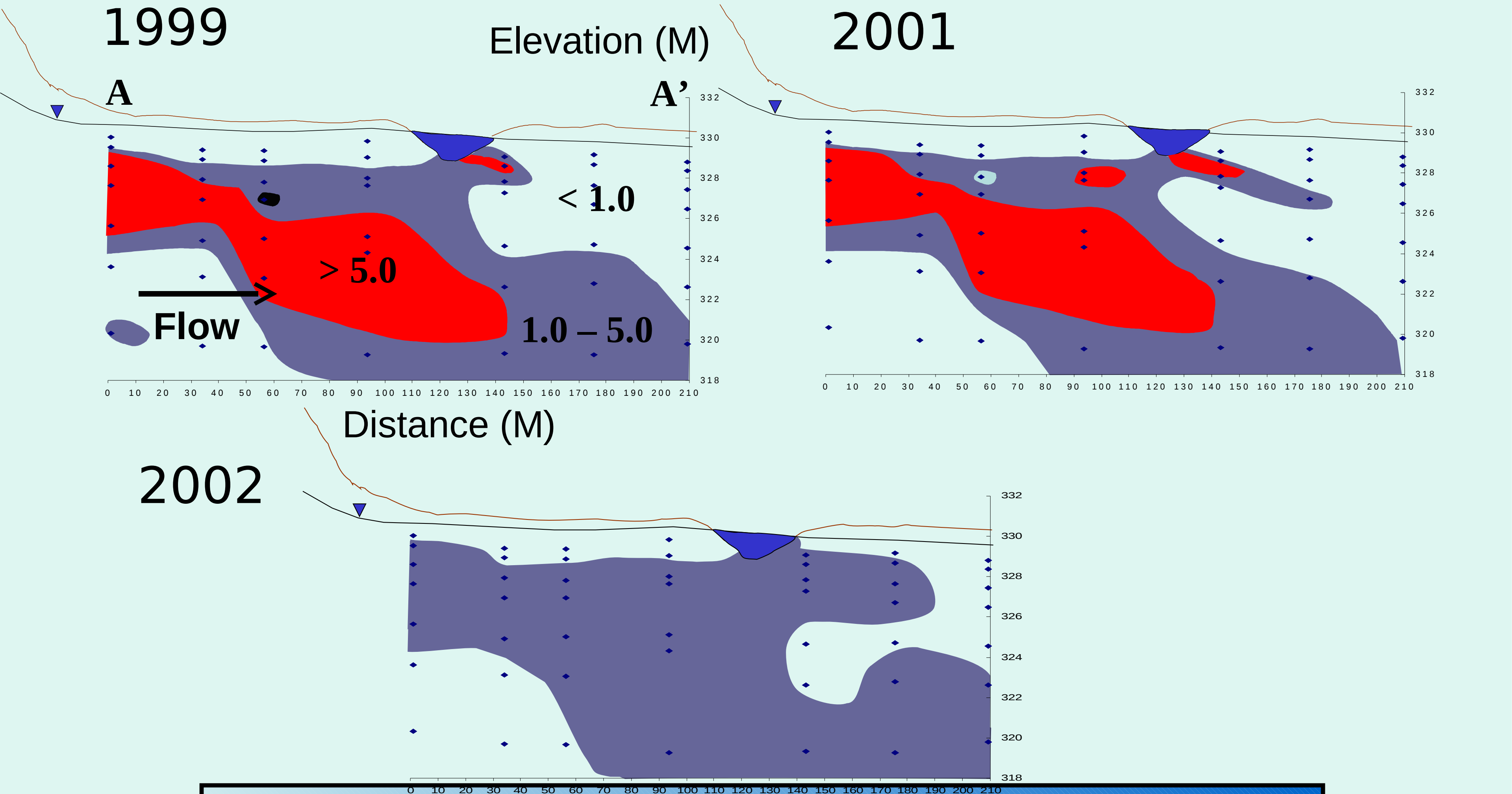
Cross Sectional View Along Plume Transect SO_4 (mg/L) 1997 through 2002



The zone of high sulfate downgradient is shrinking as the plume spreads. The Sulfate depleted plume center is expanding as degradation reactions progress.

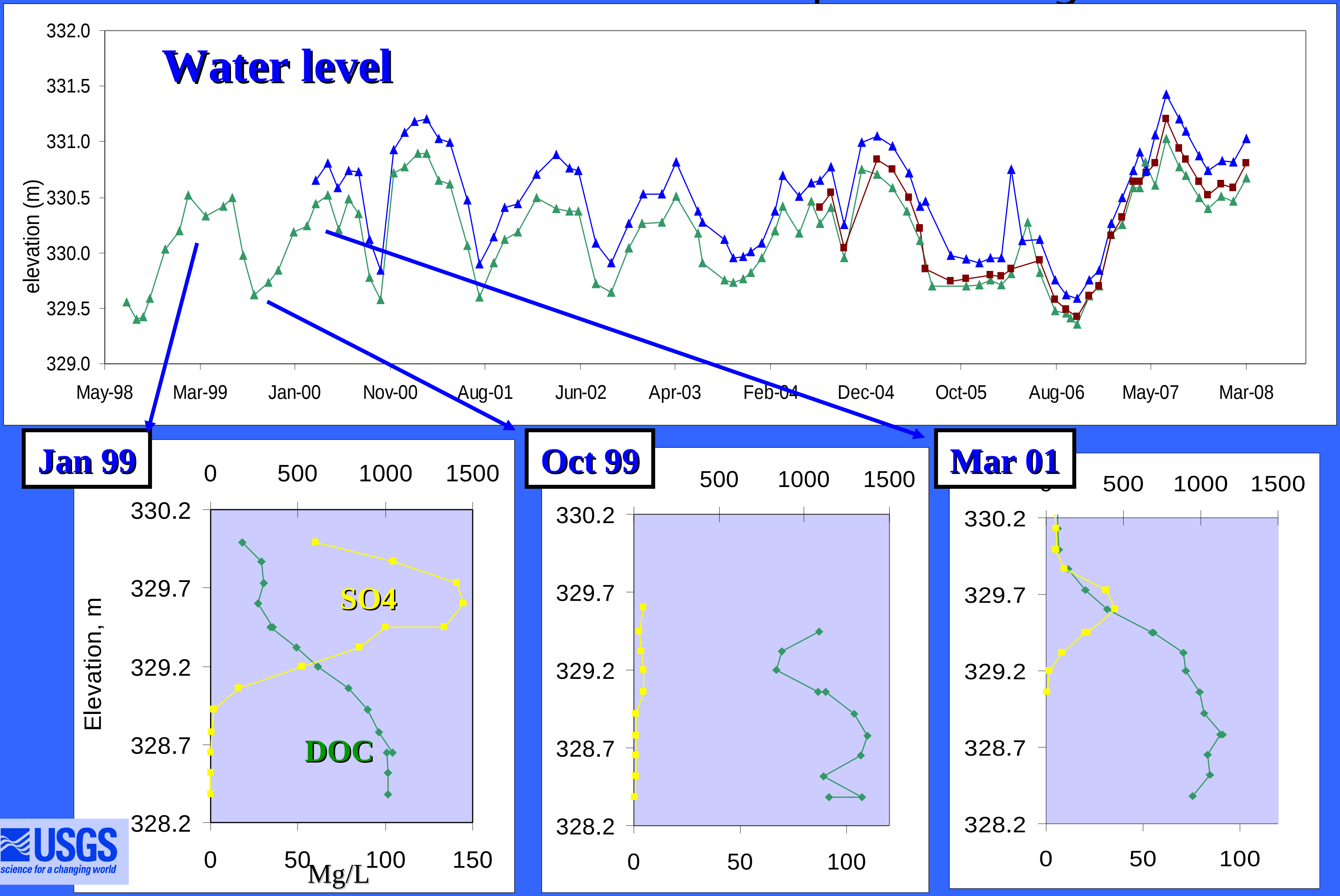
Barite dissolution provides a source of sulfate in low sulfate zones

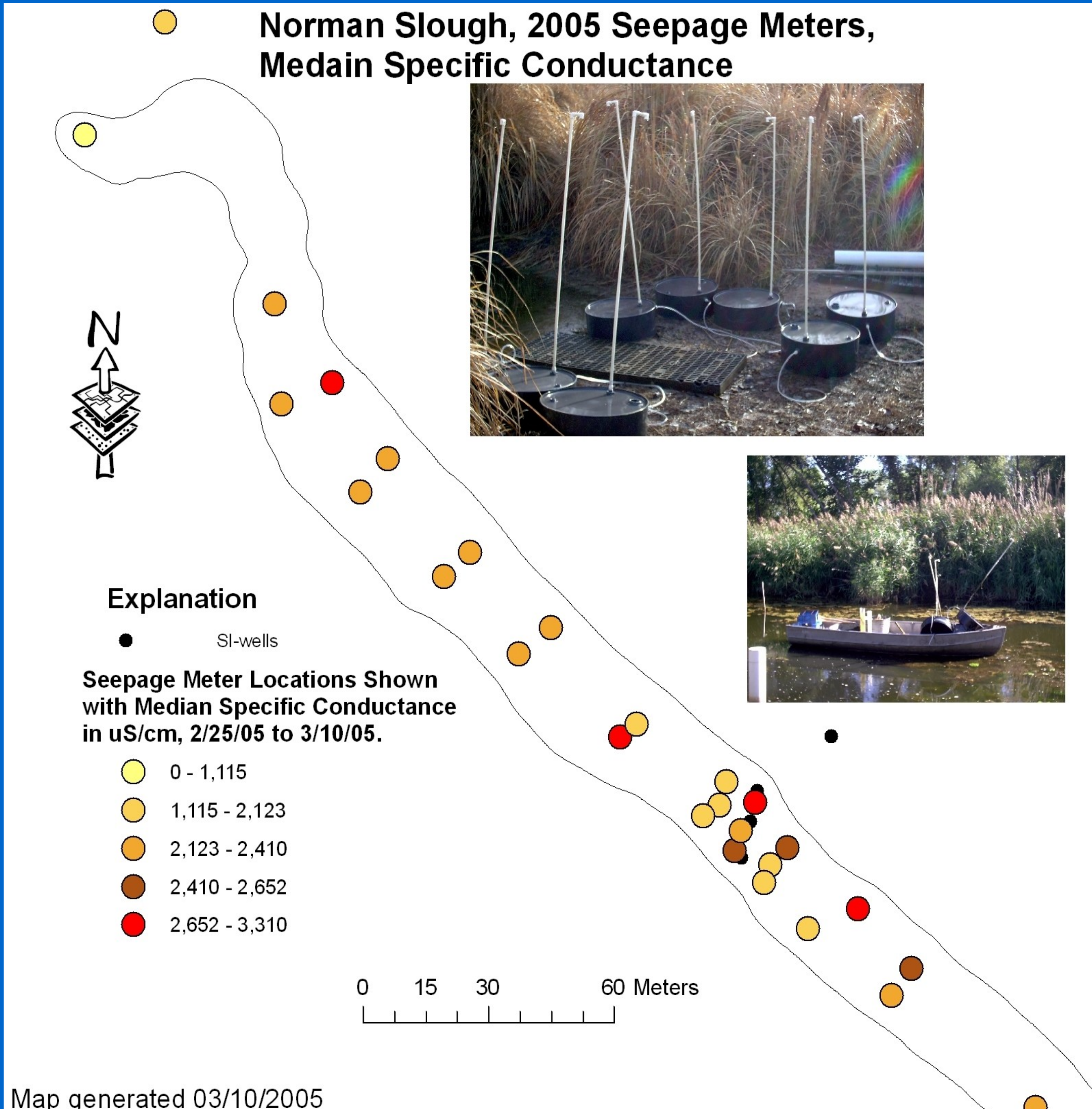
Cross Sectional View Along A-A’ Transect CH4 (mg/L) 1999 through 2002



The Sulfate Depleted Plume Center has High Methane

Water levels in the contaminant plume fluctuate over 2 meters
Sulfate infiltrates at this plume fringe





Leachate-containing groundwater discharges to the slough along the northeast bank and slough water recharges the aquifer along the southwest bank.

Presence of a discharge site (the slough) presents an opportunity to look at possible changes in important geochemical processes that impact contaminant fate. At this interface enhanced biogeochemical reactions are expected to occur.

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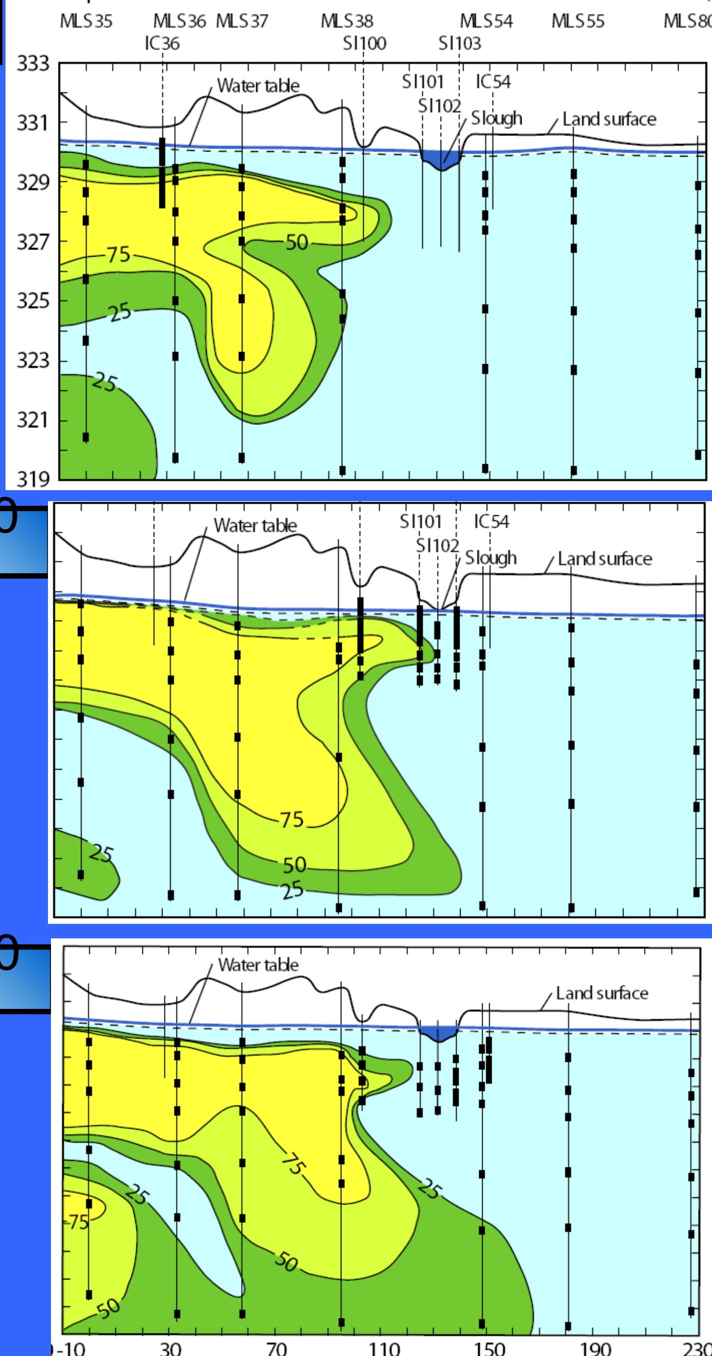
Cross Sectional View Along the A-A' Transect of NH_4 (mg/L) 1999 through 2006.

The NH_4 plume is gradually increasing in concentration and interactions with the slough sediment were investigated as a possible location of reaction-limited transport

1999

2001

2006



Elevation (m)

Distance (m)

Small-scale samples for geochemistry are collected using peepers

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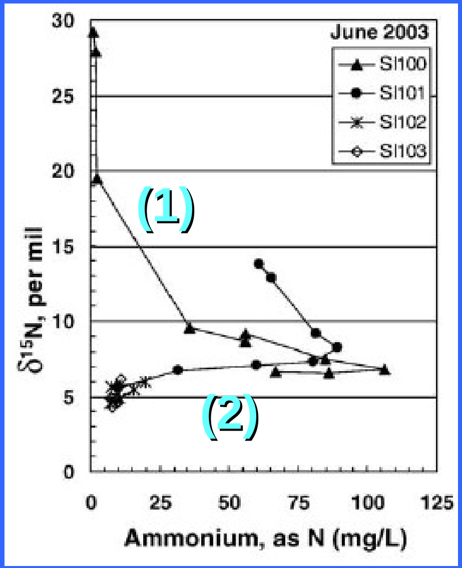
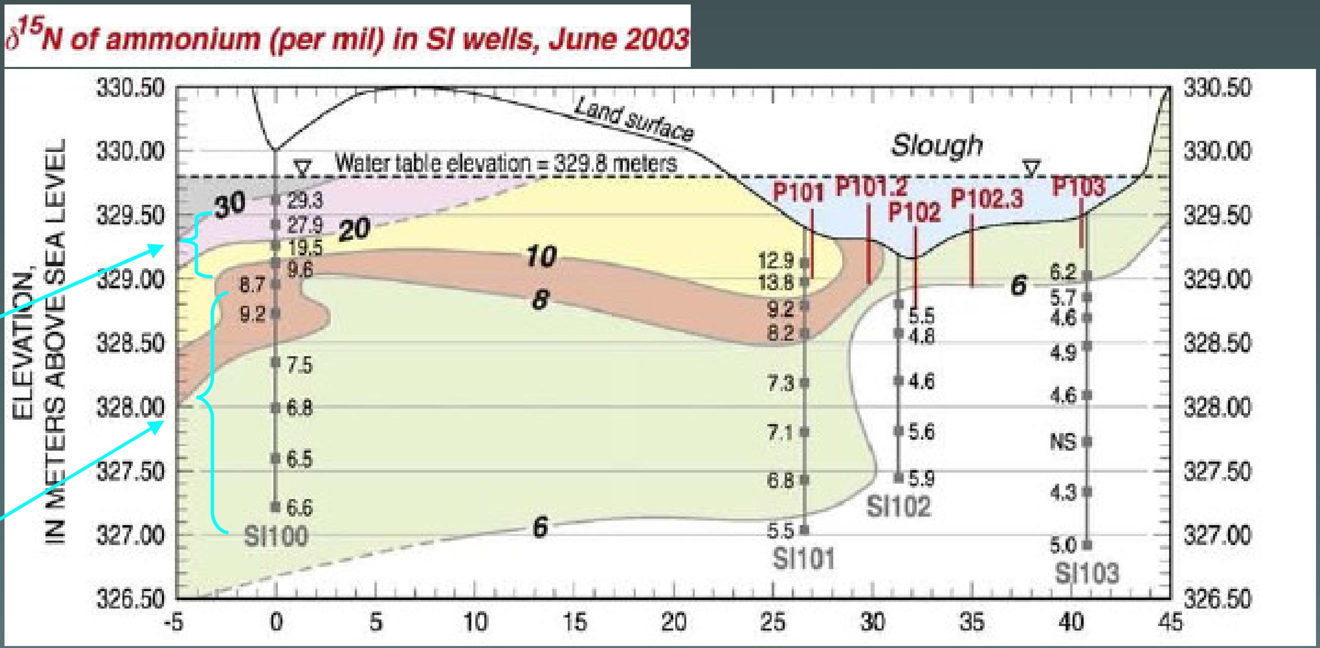
Norman Landfill

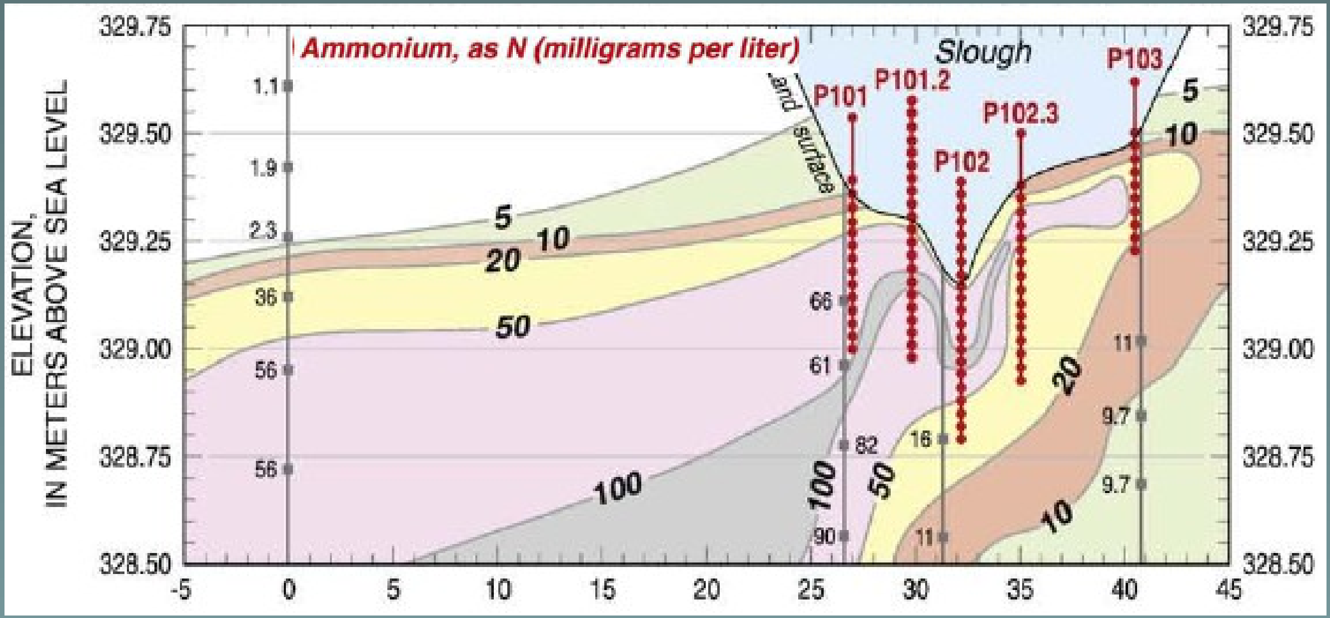
Ammonium Isotopes

(1) Increasing δ15N with decreasing ammonium indicates ammonium oxidation (nitrification)

(2) Decreasing δ15N with decreasing ammonium indicates ammonium sorption







Lorah et al., JCH

Norman Landfill

Attenuation Rates

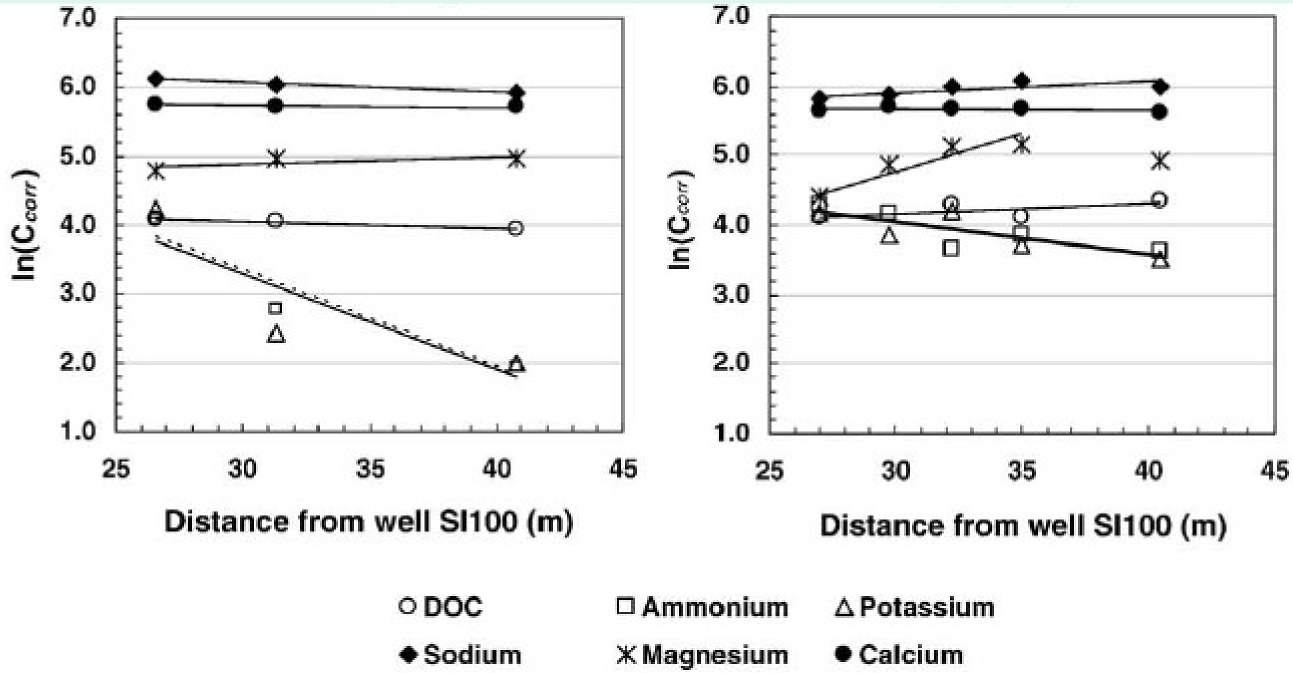
• Ammonium attenuation rate in the aquifer was about 67% higher than in the slough porewater

• Ammonium and potassium attenuation rate constants the same in aquifer and wetland indicating that sorption rather than biogeochemical processes was responsible for the attenuation of the ammonium plume

Lorah et al. JCH (2008)

Multilevel Wells | Peepers

Slope = λ, first-order attenuation rate constant with distance across the slough (m^{-1}), normalized to chloride

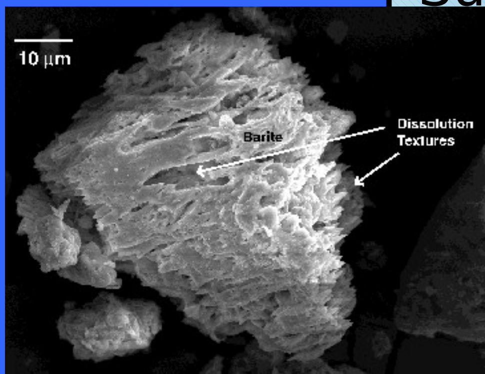


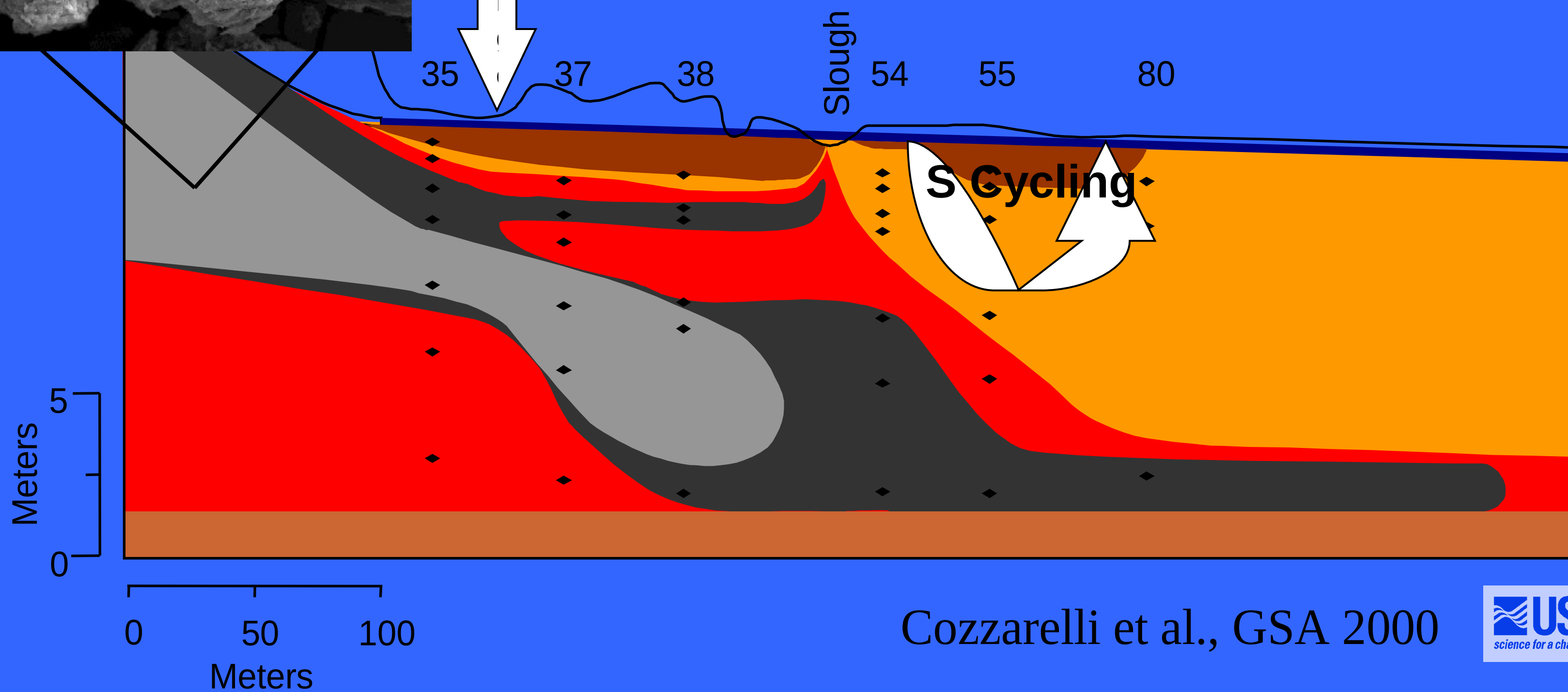
	DOC	Ammonium	Potassium	Sodium	Magnesium	Calcium
	Multilevel Wells					
Slope	-0.012	-0.142	-0.140	-0.014	0.010	-0.003
r^2	0.976	0.902	0.740	1.000	0.511	0.588
	Peepers					
Slope	0.013	-0.047	-0.047	0.034	0.094	-0.002
r^2	0.403	0.67	0.659	0.997	0.859	0.083

Microbial Incubations and Geochemical Analyses were used to Understand the Evolution of the Biogeochemical Zones

Sulfate is depleted and methanogenesis increases in center of plume

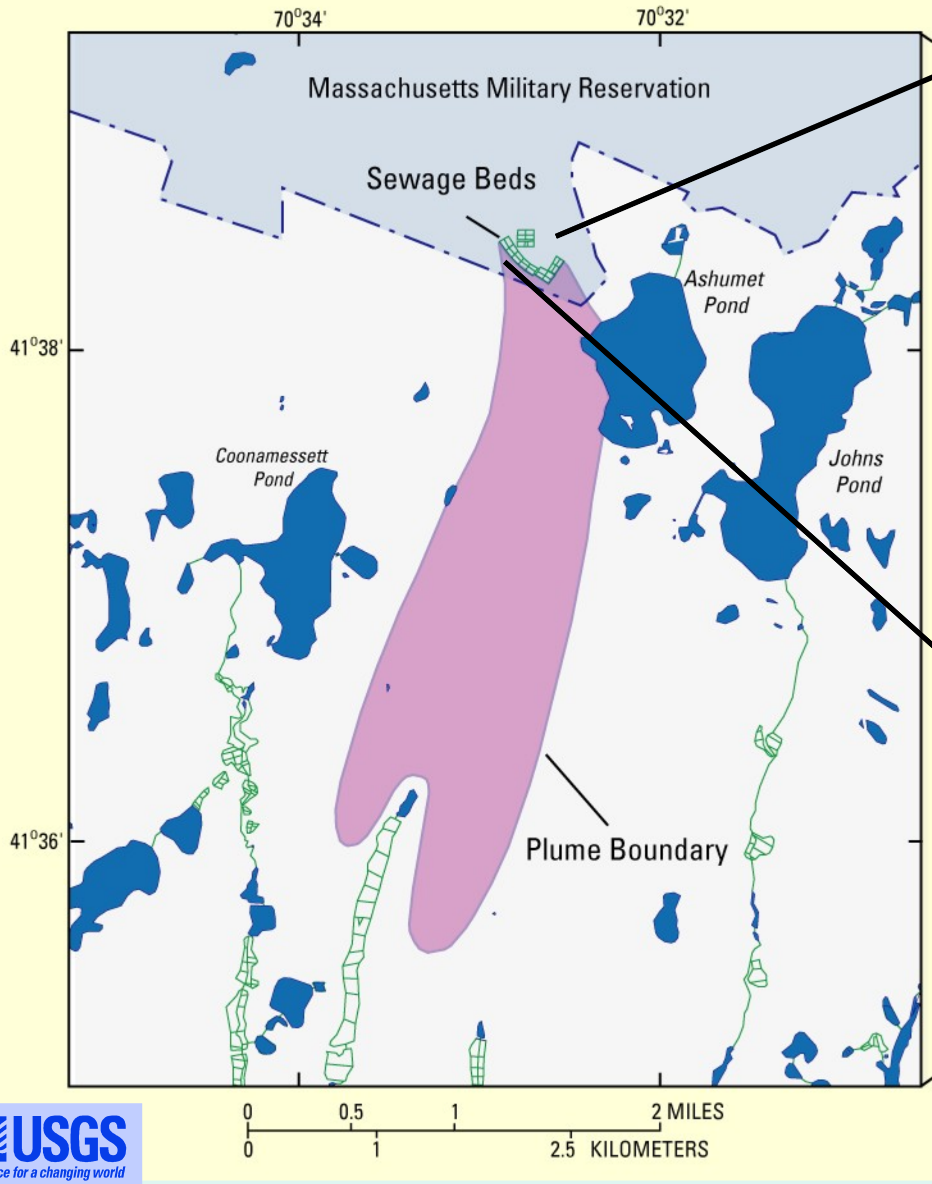
Electron acceptors are supplied by mixing at plume boundaries





Cozzarelli et al., GSA 2000

Example #3: Cape Cod Wastewater Plume



Plume was created by 60 years of disposal of treated sewage.

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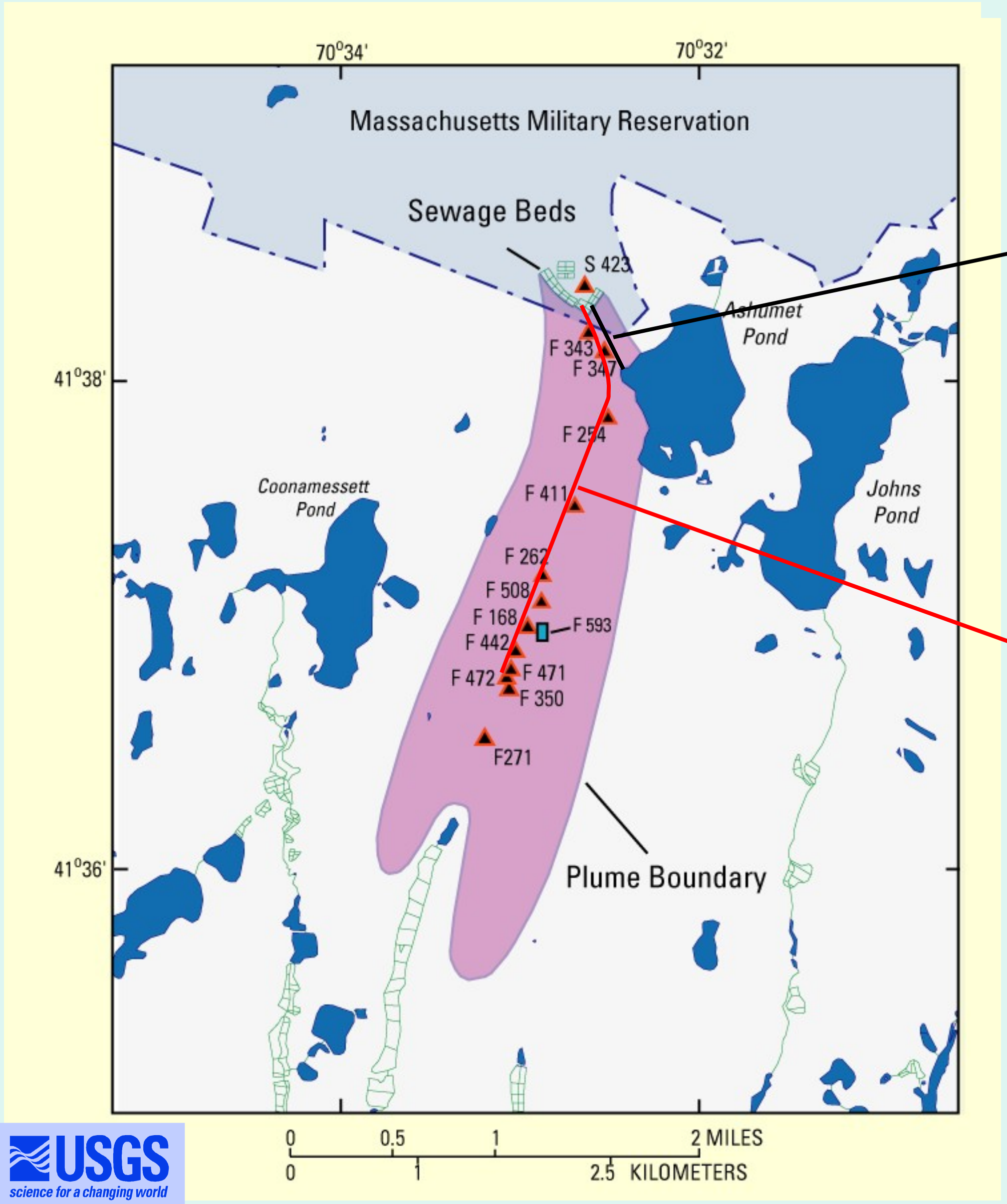
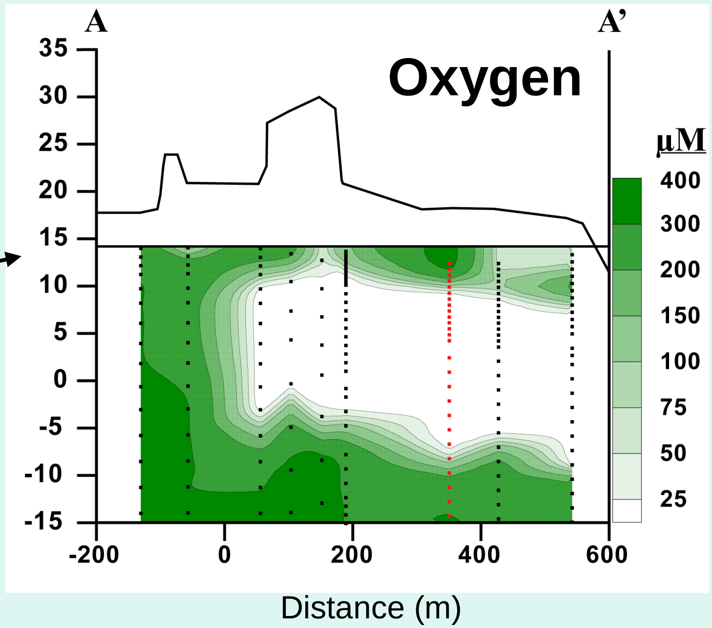
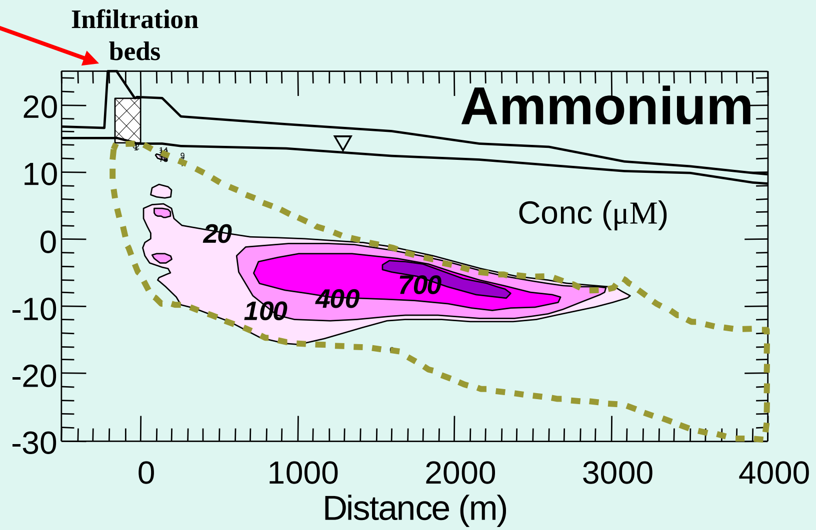
Ground Water Contaminant Plume on Cape Cod

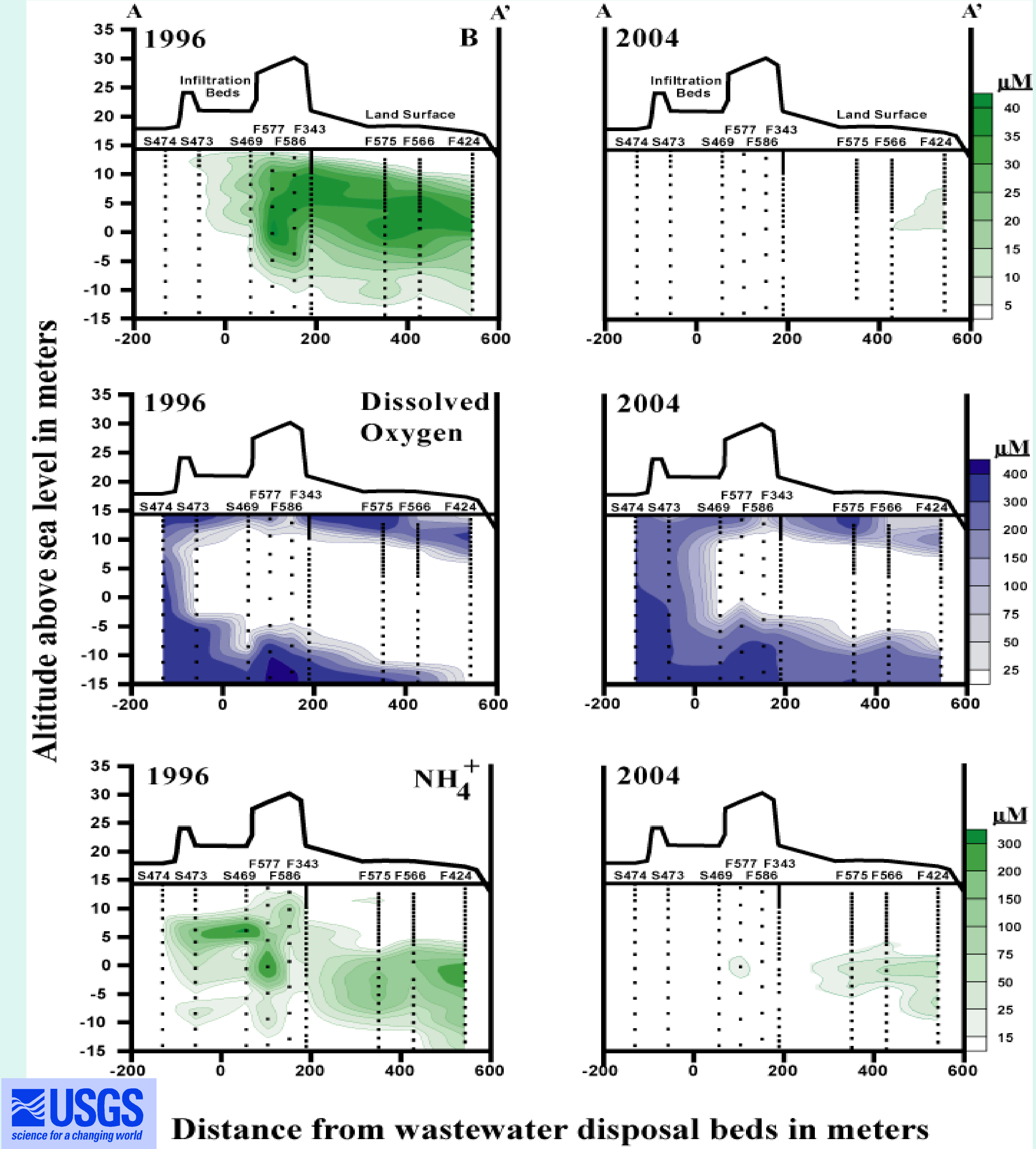






Böhlke et al. 2006 and Repert et al. 2006

After Cessation:



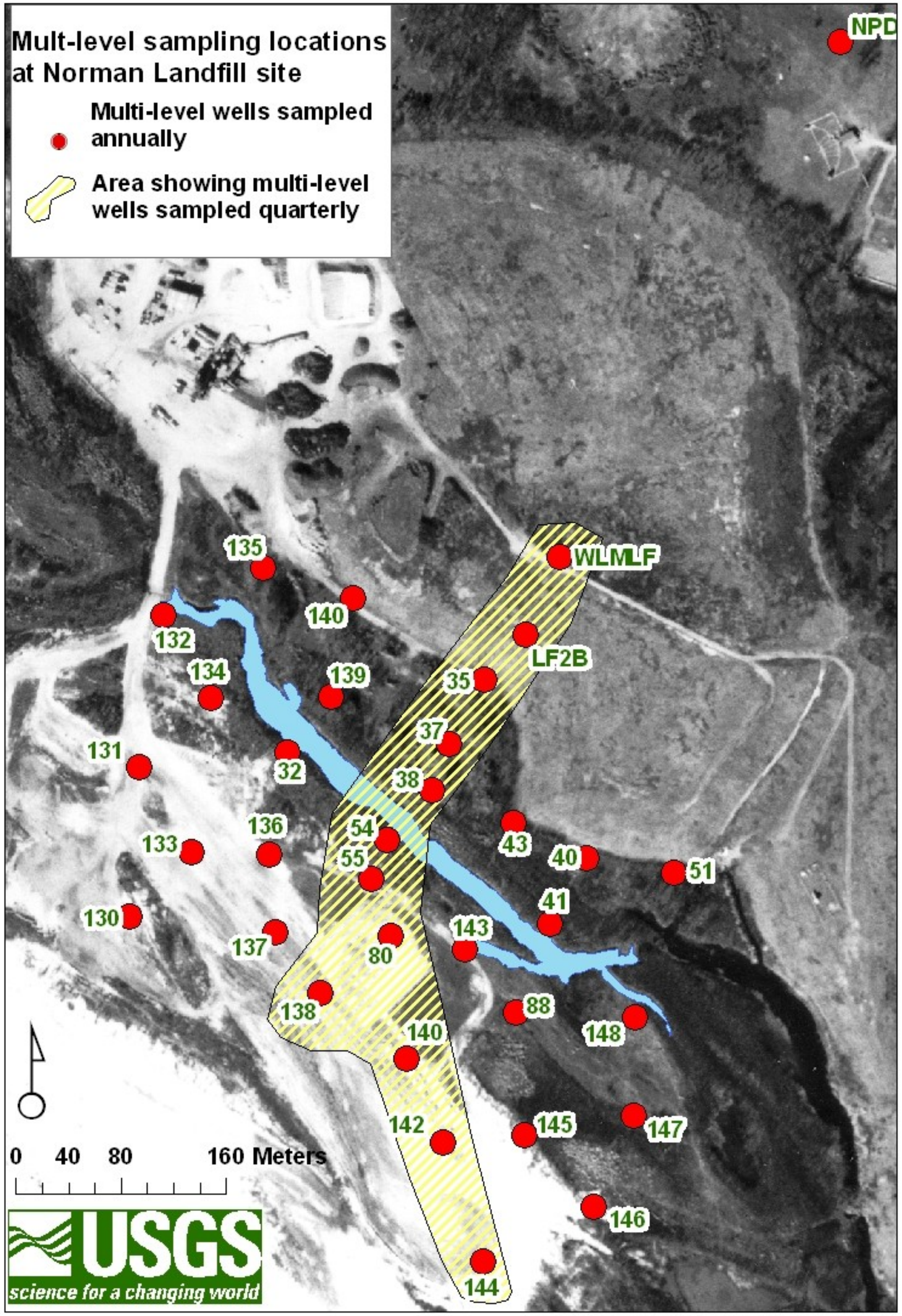
The conservative tracer, B, has flushed through the aquifer quickly

Dissolved oxygen has not mixed with the anoxic plume due to reaction with electron donors left behind on the solids

NH_4 plume remediation is slower than expected

Future direction: Coupling geochemistry and microbiology

Measuring biogeochemical processes and gene expression using GeoChip technology at Norman



Summary of GeoChip probe and sequence information by category

Gene category	No. of gene categories	No. of downloaded sequences	No. of sequences for probe design	Total no. of probes designed	Total no. of CDS covered
Carbon degradation	**24**	**18337**	**4092**	**1924**	**3192**
Carbon fixation	**5**	**4682**	**2218**	**887**	**1614**
Methane reduction and oxidation	**3**	**4134**	**1853**	**447**	**752**
Metal resistance and reduction	**43**	**28820**	**9625**	**3510**	**7021**
Nitrogen cycling	**12**	**20800**	**19229**	**4006**	**7334**
Organic remediation	**197**	**55598**	**18650**	**7093**	**12843**
Phosphorus utilization	**2**	**1876**	**1441**	**471**	**1069**
Sulfur cycling	**3**	**2523**	**2291**	**1464**	**1800**
Energy process	**2**	**2838**	**879**	**416**	**450**
Others (e.g. *gyrB*)	**1**	**8163**	**5252**	**1040**	**2089**
Total	**292**	**147,771**	**65,530**	**21,258***	**38,164**

New version covers >47,000 gene sequences of 290 gene families

The importance of the role of microorganisms in the reduction or oxidation of organic contaminants in the subsurface is well established

Investigators understand the importance of coupling geochemical measurements with microbial studies, but much work needs to be done to understand the feedback between microbial activity and geochemical conditions, including the time frame and spatial scale

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